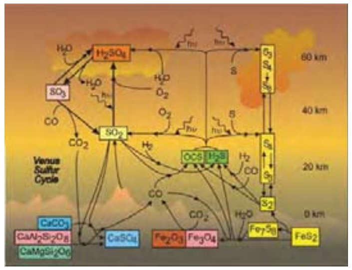
PRELIMINARY ANALYSIS OF PYRITE REACTIVITY UNDER VENUSIAN TEMPERATURE AND ATMOSPHERE

B. G. Radoman-Shaw[1], R. P. Harvey[1], N. S. Jacobson[2], G. C. C. Costa[2]
[1]Department of Earth, Environment, and Planetary Science, Case Western Reserve University, 10900 Euclid Avenue Cleveland, OH 44106 (bgs21@case.edu).
[2]NASA Glenn Research Center, 21000 Brookpark Road Cleveland, OH 44135

I. Introduction



Measurements of Venus surface chemistry suggest a basaltic composition with a predominantly CO_2 atmosphere[1]. In order to understand the reactivity of certain possible mineral species on the surface, previous simulation chambers conduct experiments at 1 atmosphere with a simplified CO_2 atmosphere[2]. Following this procedure, pyrite (FeS_2) samples are used to estimate the reactivity of sulfide minerals under a Venusian atmosphere and climate. Sulfurous gas species have been identified and quantified in the Venusian atmosphere[1], and sulfurous gas and mineral species are known to be created through volcanism[3], which is suggested to still occur on the surface of Venus[4]. This experimentation is necessary to constrain reactions that could occur between the surface and atmosphere of Venus to understand terrestrial geology in a thick and hot greenhouse atmosphere. Quantifying this reaction can lead to approximations necessary for further experimentation in more complex environments such as those in the GEER chamber at Glenn Research Center that can simulate pressure along with temperature and a more inclusive and representative Venusian atmosphere.

II. Samples

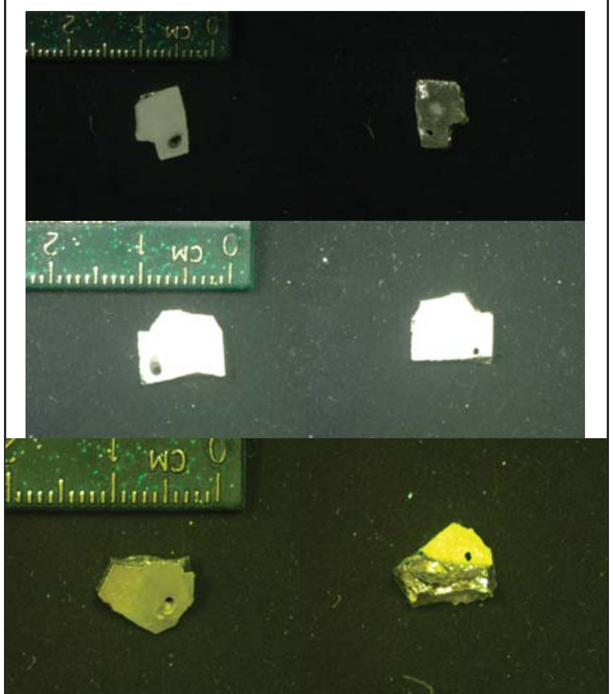


Figure 2: Samples of pyrite were supplied from the Cleveland Museum of Natural History. The three samples prepared for TGA analysis were taken from a single crystal of FeS, characterized mineralogically by XRD and a hole was cut in order to hang them in the TGA apparatus. The designation for the samples are CMNH-Pyr-R3u 5h, CMNH-Pyr-R3u 15h, and CMNH-Pyr-R3u 20h. The mass for each of the samples is 0.29284g, 0.38295g, and 0.3364g respectively. The surface area for each of the samples was calculated using ImageJ photoanalysis and the values are 2.195cm^2, 1.7876 cm^2, and 1.29 cm^2.

III. Methods

The TGA (Thermal Gravimetric Analysis) is an apparatus for measuringmass as a function of time under specific atmospheric flow conditions. For Venus approximately 94% of the atmosphere is CO_2[1]. The sample and a platinum hook was attached to a quartz rod and a platinum chain inside a quartz tube. This apparatus was balanced with separate metal weights that were also under vacuum during the experiment. The tube was then evacuated twice and the pyrite sample was subjected to a CO_2 atmosphere at a rate of 400 cm^2/min at 1 atmosphere. Temperature was then raised incrementally to typical Venus surface temperatures (470°C). The mass, temperature, and duration was monitored throughout the experiment and recorded in realtime every 10 seconds during the experiment. Any loss of mass is attributed to an oxidizing reaction of the pyrite (and other minerals) as a result of the heat and CO_2 flow.

IV. Data

Each of the samples was retrieved from the TGA intact and mass loss is attributed to discrete dust-sized particles being removed as a result of an increase in volume due to the creation of another sulfide mineral. XRD analysis of the surface of the new material shows that it is pyrrhotite, a Fe1-xS mineral. This mineral is a darker color than the pyrite and discolors the specimens. The final masses for each of the specimens in order of increased length of exposure from 5-15-20 hours are 0.29067g, 0.38003, and 0.33166g respectively. Therefore the mass loss is 0.00217g, 0.00292g, and 0.00474g respectively. The post surface area measurements are 1.406 cm^2, 3.032 cm^2, and 1.279 cm^2. This means that the surface area difference for the respective samples is -0.789 cm^2, 0.5086 cm^2, and 0.011cm^2. There was a loss of surface area for the 5 hours exposure but the two other runs show an increase by varying amounts. The rates of each of the reactions were similar however they were not equal (Figure 7). The largest difference is between the R3u 5h run and the R3u 20h run although they have the most similar mass. The R3u 15h run has the largest mass and its rate is in between the 5 and 20 hour run. In each case the general shape of the sample remains even though the texture and color of the sample is much different. These exposures however are shorter than the ones that are proposed for the GEER chamber at NASA Glenn Research Center which are on the order of days/weeks. There is an increase between 5 and 20 hour run. In each case the general shape of the sample remains even though the texture and color of the sample is much different.

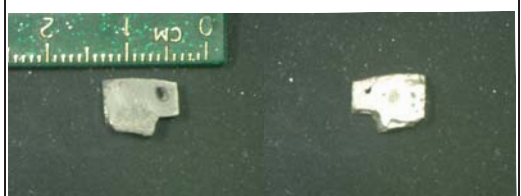


Figure 3: CMNH-Pyr-R3u 5h with scale on the A side. After exposure there is etching that occurs on the surface as well some spalation that is apparent. The over all luster of the surface has also degraded.

Figure 4: CMNH-Pyr-R3u 15h with a scale on the B side. The lack for luster for this sample as compared to the before sample is most evident due to alteration to pyrrhotite. There are also some cracks and fissures in the sample best evidenced by the cracks in the upper left side of the side A sample.

Figure 5: CMNH-Pyr-R3u 20h with a scale on the A side. The darkness of the sample is the darkest among the three pyrite samples. There is a white line of what appears to be depositional material on the A side of the R3u pyrite sample. Further analysis is necessary to determine the chemistry of this sample.

V. Discussion

The conversion of pyrite (FeS_2) to pyrrhotite ($Fe_{1-x}S$) and then Fe oxides in a hot CO_2 atmosphere (such as found at the surface of Venus) is both known and predicted from prior work; yet the relative importance of this reaction remains controversial[2,5,6]. More recent studies suggest this reaction can play a key role in buffering the abundance and oxidation state of S in that planet's atmosphere, which can differ dramatically with altitude[1,7]. Our experiments illustrate that there are some discrepancies that can occur through length of exposure suggesting mineral textures and volume changes can play key roles. Pyrrhotite was also the only major product of our experiments which was varified with XRD. The cracks in the samples, especially in R3u 15h, are most likely due to volume changes associated with newly formed minerals. It is most likely more evident in this sample becauseit underwent the largest increase in surface area 0.6638cm2. The sample with the decrease in surface area is R3u 20h (Figure 5) and this sample also has the roughest surface area on the backside of the sample whereas R3u 15h and R3u 5h are the smoothest. The heaviest sample is the R3u 15h sample (Figure 4) and this sample fell in between the two extremes of the differences of rate. The difference in rate is similar in magnitude and on average is 0.3 mg/hour. The mass loss increases with length of exposure showing that the pyrite-pyrhottite phase change progresses regardless of the effects of texture and shape.

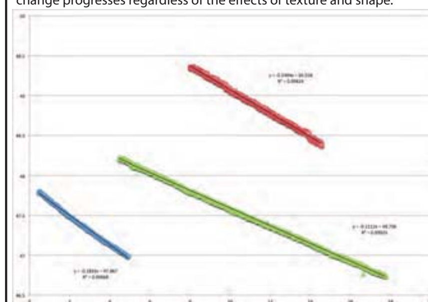


Figure 7: All pyrite samples weight versus time for the different exposures. This provides an estimation of the reaction rate from pyrite (FeS_2) to pyrrhotite ($Fe_{1-x}S$).

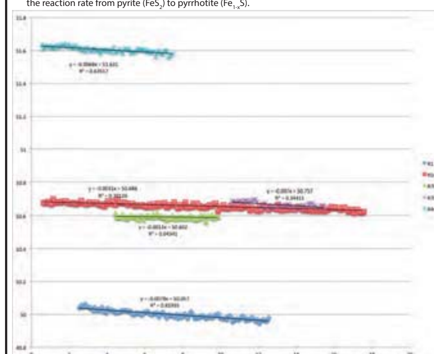


Figure 8: Reaction rates of other minerals analyzed with TGA. All of the other minerals were exposed for 20 hours similar to the longest pyrite exposure. R1 is diopside, R5n is olivine, R7bb is enstatite, and R4m is oligoclase. These mineral compositions were varified with powder XRD analysis.

VI. Further Work

The depth and chemical profile of this reaction within the charges will be examine by SEM and FIB. Other volcanic minerals such as olivine, pyroxene and feldspar are also going to be analyzed before exposure in the GEER chamber under the full Venus conditions which could force this reaction to increase or decrease in rate as well as product which might be other than pyrrhotite. Preliminary resutls show mass loss on olivine and diopside even at 1 bar which was not forseen. Further chemical modeling is necessary to pinpoint the mechanisms and reactions that are ocurring during exposure. The inclusion of SO2 at 180 ppm[1] (detected abundance in the Venusian atmosphere) will offer further insight into these oxidation reactions.

[1] Bullock M. A. and Grinspoon D. H. (2013) Comparative Climatology of Terrestrial Planets, 19-54. [2] Fegley B. Jr. et al. (1995b) Icarus 108, 373-383. [3] Krasnopolsky V. A. and Lefèvre (2013) Comparative Climatology of Terrestrial Planets, 231-275. [4] Smrekar S. E. et al. (2010) Science 328, 605-608. [5] Hashimoto G.L. and Abe Y. (2005) Planetary and Space Science 53, 839-848. [6] Wood J.A. (1997) Venus II, 637-664. [7] Treiman A. H. and Bullock M. A. (2012) Icarus 217, 534-541